NRL Report 7637

Trace Metal Water Pollutants Determined by X-Ray Fluorescence

P. G. BURKHALTER

X-Ray Optics Branch
Nuclear Sciences Division

August 7, 1973

NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

ABSTRACT

X-ray fluorescence analysis was evaluated for determining trace metals in samples of interest in the Water Quality Control Program. A number of toxic elements including Pb were determined in Potomac River water and Blue Plains sewage sludge. Analysis by x-rays has sufficient detectability to determine both insoluble and soluble pollutants in river water and effluent waste.

PROBLEM STATUS

This report is an interim report by the X-Ray Optics Branch on one phase of the problem; work is continuing on other phases of the problem.

AUTHORIZATION

NRL Problem P04-04
Project RR 011-07-41-4951

Manuscript submitted July 16, 1973.

TRACE METAL WATER POLLUTANTS DETERMINED BY X-RAY FLUORESCENCE

P. G. Burkhalter

INTRODUCTION

X-ray fluorescence (XRF) has become a well established analytical method.[1, 2] Recently this technique was evaluated for determining the concentration of elements above atomic number 12 (Mg) in particulate matter filtered from the atmosphere or from emission sources.[3, 4] In a similar fashion the x-ray technique is applicable to the particulate material filtered from water, sediment and sewage sludge. In addition, it is possible to measure the soluble salts in water by reacting them with ion-exchange resin-impregnated filter papers.[5, 6]

The Environmental Protection Agency (EPA) has published a manual for the chemical analysis of water[7] which defines the elements of interest as Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd and Pb. Concentration ranges of interest vary from a few ppb in "clean" water to about a ppm in effluent waste. Sewage sludge may contain some of these elements at levels up to a few percent.[8]

In the EPA manual for water quality control, atomic absorption spectroscopy and colorimetry are the methods recommended for trace metals. Atomic absorption is directly applicable for determining the dissolved ions; additional steps are required to place the particulate material in solution. In some cases chelating agents and organic extractions are necessary.[9]

XRF can perform multi-element analyses in a few minutes; samples are collected easily on filter paper or ion-exchange paper, and they are not destroyed during the analysis. Blasius, et al.[10] have used XRF to analyze samples from the Miami River; detection limits of 20-30 ppb were achieved but the measurements required counting for hours because radioisotopes were used for excitation. In the work described in this report, samples of river water and sewage were analyzed using x-ray tube excitation which gives intensity three or four orders of magnitude greater than radioisotopes, thus permitting correspondingly shorter counting times.

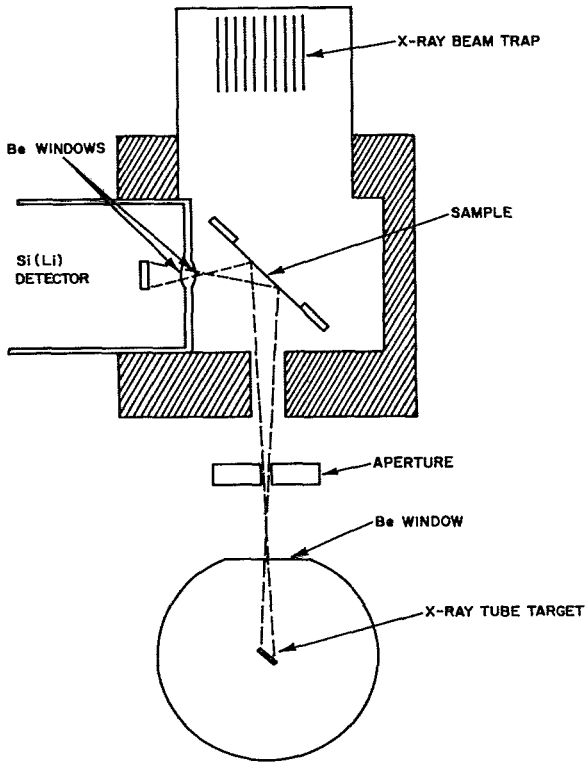

Fig. 1 — Schematic diagram of energy dispersion x-ray apparatus

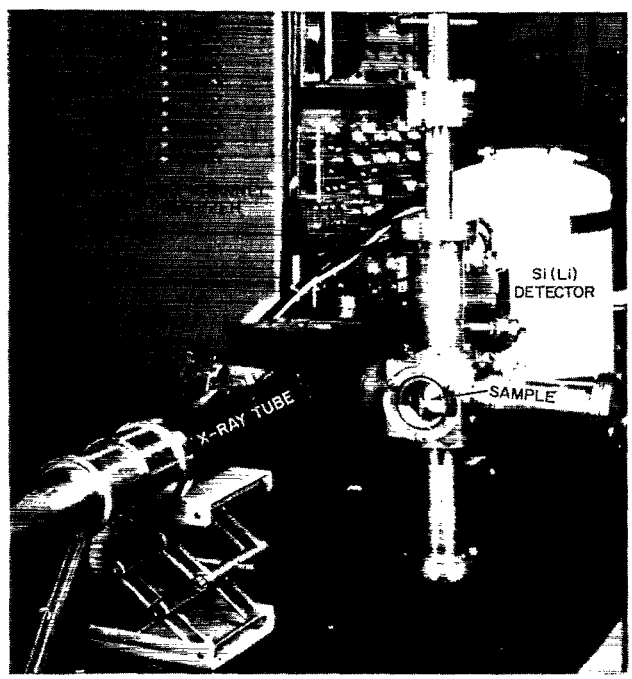

Fig. 2 — Photograph of energy dispersion apparatus at NRL

INSTRUMENTATION

The energy dispersion x-ray analysis system used in this work is shown schematically in Figure 1; it consists of a standard Si(Li) semiconductor detector having an energy resolution of 200 eV at MnKα (5.9 keV), an apertured x-ray tube illuminating about a square centimeter of sample, a vacuum chamber to eliminate air scattering of the primary beam, and a means of changing samples without breaking vacuum. The beam trap minimizes scattering of the primary beam after it is transmitted through the thin sample. The counting electronics include a multichannel analyzer for recording and digitizing the x-ray spectrum. Figure 2 is a photograph of this equipment. It is estimated that this x-ray analyzer, including x-ray generator, could be duplicated for about $25,000.

EXPERIMENTAL

The sensitivity (slope of the x-ray intensity versus elemental concentration calibration curve) was determined from single-element standards prepared by depositing known amounts of soluble salts on filter paper. An EPA-provided multi-element solution containing known amounts of the elements of interest was prepared in the same way to confirm the validity of the calibration.

Types of Samples

A specimen of Potomac River water was filtered through 0.8 μ Millipore to collect the particulates. The water, now clear, was acidified with HCl to a pH of about 2, and was passed seven times through a Reeve Angel SA-2 cation exchange paper to collect the dissolved ions. The ions from one of the EPA multi-element solutions were collected on ion-exchange paper in a similar fashion.

Samples of sewage sludge were obtained from the Blue Plains Sewage Treatment Plant adjacent to the Naval Research Laboratory (NRL). A few milligrams of solids were filtered onto the millipore paper without difficulty.

Measuring Spectra

X-ray spectra were collected for 100 seconds for each of the samples (except for one of the EPA solutions). The Ni-filtered W target x-ray tube was operated at 48 kV, 8 mA, which produced a total count rate about 2500 c/s from the sample. X-ray line intensities were integrated over their full-width at half-maximum and the background was integrated over an equal energy range adjacent to the peak. However, for the ion-exchange papers, the background was determined on a blank substrate.

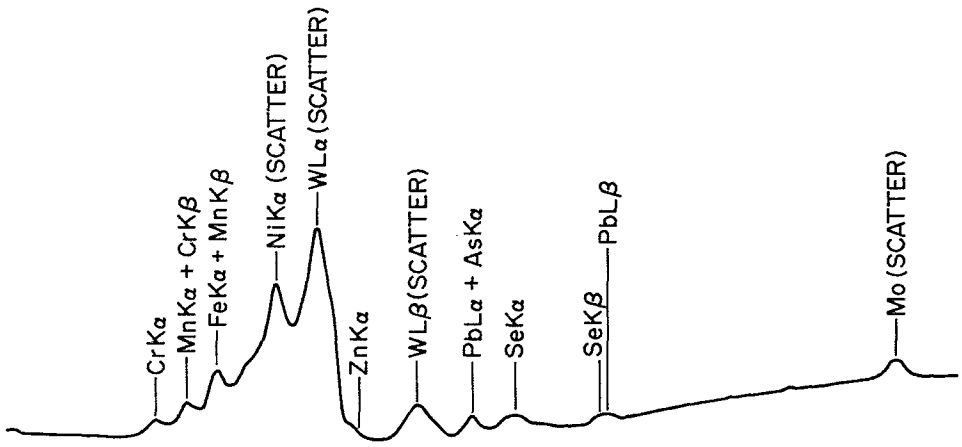

Fig. 3 — XRF spectrum of EPA multielement solution deposited on filter paper

TABLE I
EPA Reference Standard
(solution evaporation on filter paper)

Element	EPA Value ng/cm^2	Measured XRF ng/cm^2
Al	850	ND*
Cr	310	320
Mn	340	330
Fe	590	490
Zn	280	80
As + Pb	480	470
Se	40	20
Cu	240	ND†
Cd	60	ND

*ND not detectable

†Cu not detectable due to scattered W interference.

RESULTS AND DISCUSSION

The 400 second x-ray spectrum of the EPA multi-element solution deposited on filter paper is shown in Figure 3 and the results of the x-ray analysis compared to the known concentrations are listed in Table I.

The spectra for the particulate material filtered from the Potomac River water and for the soluble elements collected by ion-exchange paper are shown in Figures 4 and 5, respectively; the results of the analysis are presented in Table II. Figure 6 shows the spectrum for the EPA solution passed through ion-exchange paper. These x-ray results are compared with known concentrations in Table III. The spectrum for the sewage sludge is shown in Figure 7, and in Table IV the x-ray results are compared with atomic absorption analyses of similar samples (taken from the same location but at different times[8]).

The results demonstrate that most of the elements of interest in water and sludge samples can be measured easily by XRF. Good agreement with known concentration was obtained for the EPA solution deposited on filter paper, with the exception of Zn. The x-ray results on the sewage sludge agree within about a factor of two with atomic absorption analyses even though the samples were collected at different times. Unfortunately, no independent data are available for the pollutant concentration in the Potomac River so no further comparisons can be made.

There were some minor limitations in these particular XRF measurements due to adapting existing instrumentation. For instance, the energy dispersion x-ray analysis system was not designed to measure the low-energy x-ray lines characteristic of the low atomic number elements; hence, no data are shown for Al. It would not be difficult to measure light elements (down to Al or Mg) with a similar x-ray system using thinner windows and possibly having the x-ray tube and detector contained within the vacuum to avoid air absorption. At the other end of the spectrum, high energy x-rays are not efficiently excited by an x-ray tube operated near 50 kV. Cd is one such element; its sensitivity, and hence its detection limit, suffers because of the limited excitation. It was not detected in any of the samples. Operation of an x-ray tube at or above 60 kV might be expected to improve the detection limit to the extent necessary to measure Cd successfully. A Mo target tube would provide more efficient excitation of As and eliminate the W scatter interference with Cu (see Figure 5).

When using a Si (Li) detector with a pulse resolution of 200 eV, line intensity overlap can occur in certain x-ray regions. For $19 < Z < 26$, the Kβ of one element cannot be separated from the Kα of the next higher atomic number. The sewage sample spectrum (Figure 7) illustrates the interference between V Kα and Ti Kβ; the larger concentration of Ti makes it impossible to measure the amount of V present without resorting

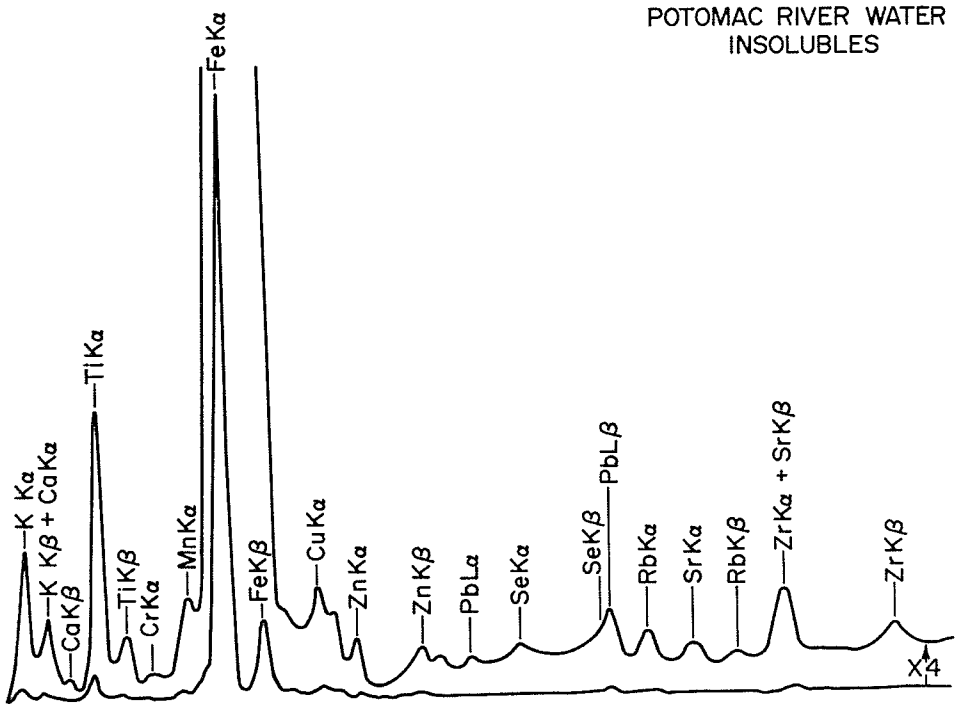

Fig. 4 — XRF spectrum of Potomac River water particulates

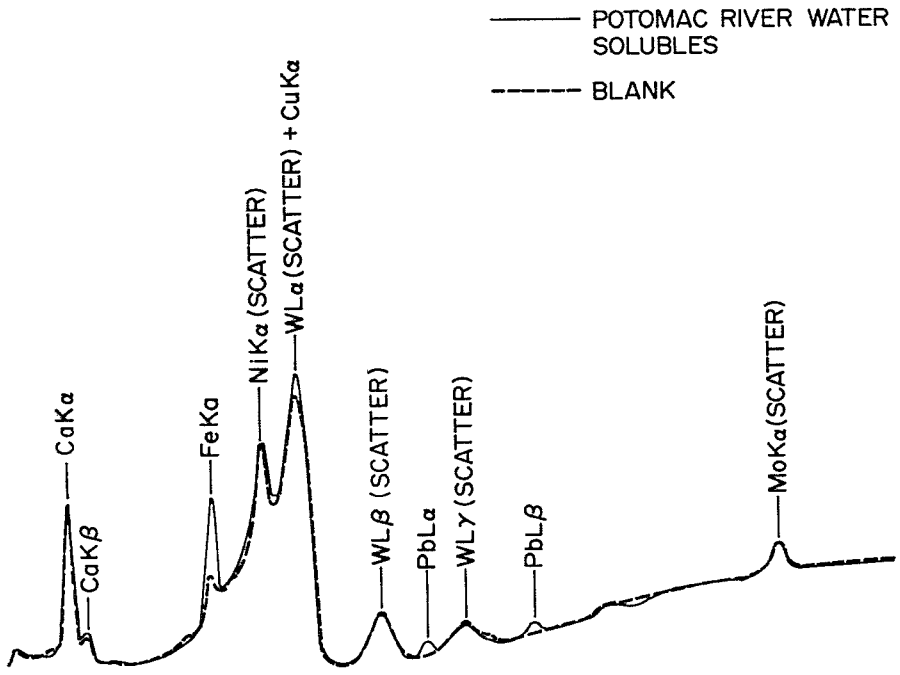

Fig. 5 — Spectrum of ions extracted from Potomac River water by ion-exchange paper

TABLE II
Potomac River Water

	Insolubles ppm of total solids	Solubles ppm in water
K	420	
Ca	180	
Ti	600	
Cr	10	
Mn	70	
Fe	7700	0.23
Cu	30	.07
Zn	50	
Se	10	
Pb	20	.05
Zr	330	

TABLE III
EPA Reference Standard for River Water
(by ion exchange)

X-Ray	EPA Value $\mu g/cm^2$	Measured XRF $\mu g/cm^2$
Cr Kα	6.6	7.3
Mn Kα	7.7	4.7
Fe Kα	32	34
Cu Kα	5.4	2.0
Zn Kα	6.3	3.6
Pb Lβ	7.4	5.1
As Kα	5.8	ND*
Se Kα	1.3	.3
Cd Kα	1.3	ND

*ND not detected

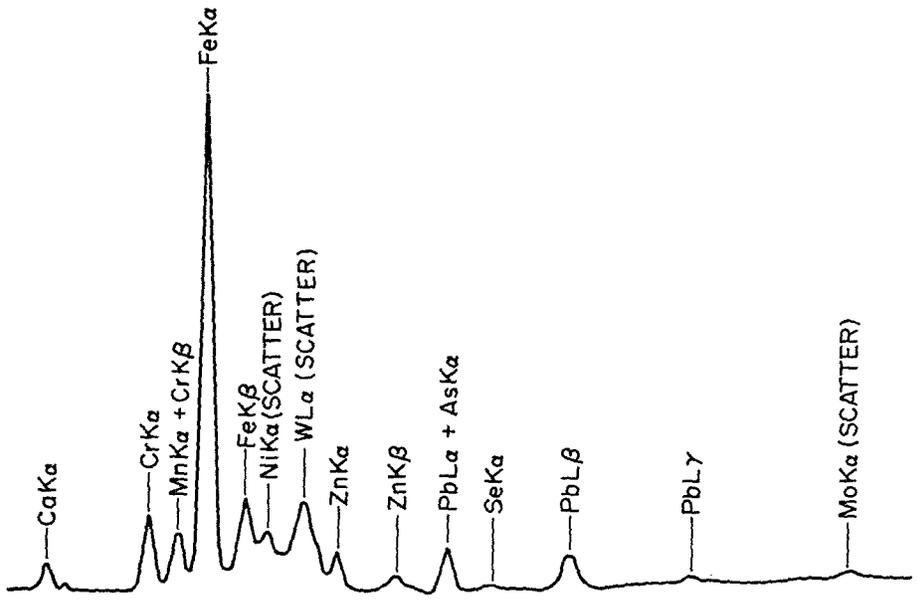

Fig. 6 — Spectrum of elements extracted from EPA multi-element solution on ion-exchange paper

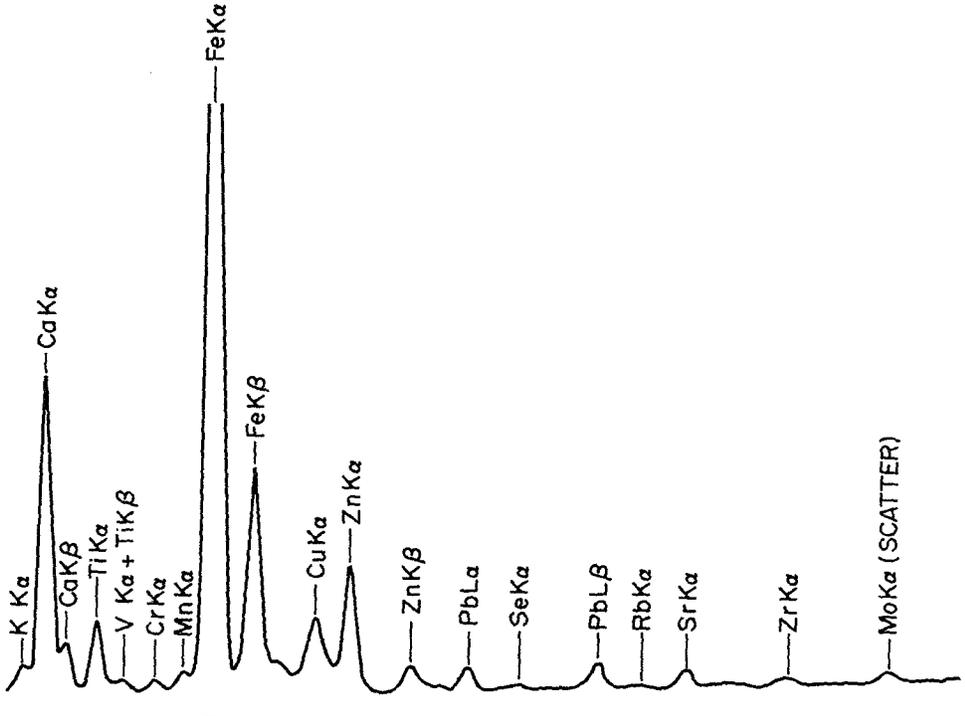

Fig. 7 — XRF spectrum of Blue Plains sewage solids

to sophisticated computer stripping. This type of interference can be avoided by using a crystal spectrometer for which the resolution ranges from 4 to 20 eV between K and Fe and is adequate to eliminate the Kα-Kβ overlap. Crystal-spectrometer x-ray analyzers are described in the Appendix.

Overlap of K- and L-series lines can also cause interference for certain elements. One of the most severe cases, As Kα and Pb Lα, cannot be resolved even by a crystal spectrometer because their energies differ by only 6 eV, and in this energy region the resolution of a crystal spectrometer is about 60 eV. If both As and Pb were present, x-ray analysis would be performed by measuring the As Kβ and Pb Lβ. This poses something of a problem for As because the Kβ line is only about one-fifth as intense as the Kα line; hence the detection limit is degraded. Furthermore, if Hg is present, Hg Lβ will interfere with As Kβ.

The ion-exchange collection of soluble elements, Table III, demonstrated complete recovery of Cr and Fe, partial recovery of Mn, Cu, Zn, Se and Pb, and no recovery of As or Cd. Other ion-exchange papers would be better for some of these elements. Further understanding of the exchange process[11] is required to determine the most efficient way to make use of this technique.

TABLE IV
Blue Plains Sewage Sludge

	XRF mg/g	AA* mg/g
Ca	8.3	20-24
Ti	12	
Cr	.2	.4
Mn	.1	.5
Fe	18.5	27
Cu	.4	.4-.9
Zn	2.2	.4-1.8
Se	.04	
Sr	.2	
Pb	.4	.2-1.1

*Atomic Absorption results from samples taken at a different time.[8]

DETECTION LIMITS

The critical factor which determines the application of a technique to a problem of microanalysis is the detection limit. This is defined as the amount of material which gives a signal above background equal to three times the standard deviation of the background. The detection limits measured in the air pollution work using the NRL single crystal spectrometer[3] and a modern multiple spectrometer instrument[12] are listed in Table V along with those measured in the energy dispersion system used in this work. When sampling the particulates from a fluid such as river water or sewage, it is important to limit the amount of material deposited on the substrate to that mass thickness which can be considered "thin", i.e. to that thickness for which absorption corrections can be neglected. For x-ray energies greater than about 6 keV, this criterion is satisfied below 5 mg/cm^2. This substrate loading can be accomplished quite readily with sewage sludge where the solids content varies from 1 to 25%. The volume of river water which leads to this thickness is a function of the cleanliness of the water; 5 mg/cm^2 of particulate material resulted from filtering 240 ml of freshly sampled Potomac River water through 10 cm^2, 0.8 μ pore size Millipore. The last column of Table V lists the range of detection limits for the different x-ray instruments in terms of micrograms of element per gram of solids. Table VI compares the detection limits in parts per billion based on 240 ml sample with the concentrations expected in three different types of water.

These detection limits were determined from single-element standards prepared by depositing solutions on filter paper. Multi-element particulate samples would suffer from increased background thus degrading the detection limit somewhat; the increase in background might be due to increased scattering caused by the mass of the particulate material and/or the tailing from an adjacent high intensity peak. With reference to Figures 4 and 7, the detection limit for Mn would be degraded by a factor of three due to the tail of the Fe-peak and the detection limit for Se and Pb would be degraded by a factor of two due to the general increase in background caused by the mass of particulate material. For light elements (below Fe) the detection limit suffers when the sample is deposited through the thickness of the substrate because of absorption of the low energy x-rays in the substrate. For Ca Kα measured from a solution deposited on filter paper or extracted on ion-exchange paper the substrate absorption reduces the x-ray intensity by about a factor of two; for Al Kα, the factor would be 20. However, neither of these perturbations on the detection limits negate the conclusion that XRF can easily analyze the trace metal concentrations that exist in dirty river water and effluent waste.

TABLE V

XRF Detection Limits

X-Ray	Energy keV	Energy Dispersion[a] ng/cm^2	Wavelength Dispersion[b] ng/cm^2	Wavelength Dispersion[c] ng/cm^2	Detection Limit Rang $\mu g/g$ of soli
Al Kα	1.49	ND*	85	5	1-20
Ca Kα	3.69	60	30	15	5-10
Cr Kα	5.41	25	35	20	5-10
Mn Kα	5.90	35	35	20	5-10
Fe Kα	6.40	45	30	20	5-10
Cu Kα	8.05	165 (W Lα Bgd)	50	30	5-30
Zn Kα	8.65	30	50	30	5-10
Pb Lα	10.5	35	260	160	10-50
Se Kα	11.2	30	150	90	5-30
As Kβ	11.7	70	200	90	15-40
Cd Kα	23.2	135	ND	ND	30

a) Measured with W x-ray tube operated at 48 keV and 8 ma with extrapolation to 10, total intensity.

b) NRL single-crystal spectrometer with Rh x-ray tube operated at 900 watts.

c) Measured in multi-spectrometer instrument with Rh x-ray tube operated at 2500 w

d) Based on a sample mass thickness of 5 mg/cm^2.

*ND not determined

TABLE VI
Typical Concentrations in Water Samples
(ppb)

Metal	Clean Water	River Water	Effluent Waste	XRF Detection Limits[a)]
Al	25	600	1100	0.2-4
Cr	9	80	400	1-2
Mn	10	100	450	1-2
Fe	20	400	800	1-2
Cu	9	70	300	1-6
Zn	10	80	350	1-2
Pb	30	900	350	2-10
Se	5	20	50	1-6
As	20	70	300	3-8
Cd	2	20	70	6

a) Based on filtering particulates from 240 ml of river water.

CONCLUSIONS

XRF analysis is usable for multi-element determinations of trace metals in polluted waters. Both particulates and soluble trace metals in river water and sewage sludge can easily be sampled on filter papers which are convenient for use in x-ray equipment. The detectable limits for many pollutants with atomic numbers ranging from Ca to Pb are in the 1-10 ppb range for particulates filtered from river water and in the 5-15 ppb range for soluble trace metals extracted by ion-exchange papers. However more work is necessary to study the use of ion-exchange papers and interferences in actual multi-element samples and to establish the best conditions for XRF of water pollution samples.

Individual manufacturers could monitor their own pollution by periodic sampling on filter paper which can be sent to a central laboratory for analysis. Either a fully automated, multi-spectrometer x-ray machine or a computer-equipped energy dispersion detector in a central laboratory can provide rapid, low cost x-ray analysis of air, water, and sewage pollution samples.

ACKNOWLEDGMENTS

The author wishes to acknowledge the helpful discussions with L. S. Birks and J. V. Gilfrich and their assistance in preparation of the manuscript.

REFERENCES

[1]L. S. Birks, "X-Ray Spectrochemical Analysis," 2nd Ed., Wiley-Interscience, N. Y., 1969, pp. 143.

[2]E. P. Bertin, "Principles and Practice of X-Ray Spectrometric Analysis," Plenum Press, N. Y., 1970, pp. 679.

[3]J. V. Gilfrich, P. G. Burkhalter, and L. S. Birks, "X-Ray Spectrometry for Particulate Air Pollution: A Quantitative Comparison of Techniques," to be published in Anal. Chem., Oct. 1973.

[4]L. S. Birks, J. V. Gilfrich, and P. G. Burkhalter, "Development of X-Ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions," EPA-R2-72-063, Nov. 1972, pp. 28.

[5]C. L. Luke, "Ultratrace Analysis of Metals with a Curved Crystal X-Ray Milliprobe," Anal. Chem. 36, 318 (1964).

[6]W. J. Campbell, E. F. Spano, and T. E. Green, "Micro and Trace Analysis by a Combination of Ion Exchange Resin-Loaded Papers and X-Ray Spectrography," Anal. Chem. 38, 987 (1966).

[7]"Methods for Chemical Analysis of Water and Wastes," EPA-16020, Cincinnati,Ohio, Aug. 1971.

[8]EPA Task Force, "Sewage Sludge Incineration," EPA-R2-72-040, Aug. 1972.

[9]"Standard Methods for the Examination of Water and Wastewater," 13th Edition, American Public Health Association, 1971, pp. 210-215.

[10]M. B. Blasius, S. J. Kerkhoff, R. S. Wright, and C. R. Cothern, "Use of X-Ray Fluorescence to Determine Trace Metals in Water Resources," Water Resources Bulletin, 8, 704 (1972).

[11]T. E. Green, S. L. Law, and W. J. Campbell, "Use of Selective Ion Exchange Paper in X-Ray Spectrography and Neutron Activation Application to the Determination of Gold," Anal. Chem. 42, 1749 (1970).

[12]L. S. Birks and J. V. Gilfrich, Report to EPA, "Development of X-Ray Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emission; Phase II: Evaluation of Commercial Multiple Crystal Spectrometer Instruments," NRL Report 7617, June 1973.

APPENDIX

High resolution, crystal-spectrometer-type x-ray instruments are commercially available which could be used to monitor trace elements in water pollution. At NRL we have a vacuum, crystal-spectrometer x-ray instrument capable of 50 kV operation up to 1900 watts. A schematic illustration of wavelength dispersion using a crystal spectrometer is shown in Figure A-1. This spectrometer was used to determine 100-second x-ray detection limits for a large number of elements in the air pollution study[3] but requires re-setting the spectrometer and detector for each element.

This time-consuming single element determination is eliminated with the newer multi-spectrometer instruments capable of simultaneous determinations of 14 to 24 elements with automatic data processing and print-out. These machines use state-of-the-art, high-powered x-ray tubes producing excellent x-ray sensitivities. Such an instrument is illustrated schematically with a few spectrometers and a semiconductor detector in Figure A-2. While the spectrometers are fixed to measure certain x-rays, the Si (Li) detector can look for all elements present and catalogue the spectral data for a given sample; this data could be processed later for elements of importance in fingerprinting a particular polluter. Automatic loading and processing of data would allow complete determination in 2 or 3 minutes per sample. With the use of a dedicated computer, the x-ray intensities can be processed for background subtraction, have matrix absorption corrections if necessary, and be converted to concentrations for the final print-out of a permanent record of all the elements in the sample. The basic cost of a multi-spectrometer instrument is about $100,000. Additions of the Si (Li) detector, automatic sample handling, and data processing probably would add about $30,000 to the cost. This instrumentation appears justifiable and probably the most sensible means of processing large numbers of air or water pollution samples in a central laboratory. Processing one sample every two minutes continuously for 40 hours per week using automatic equipment, one can estimate cost for analyzing all heavy metals to be $1.50 per sample[3], including amortization of the equipment over a five-year period.

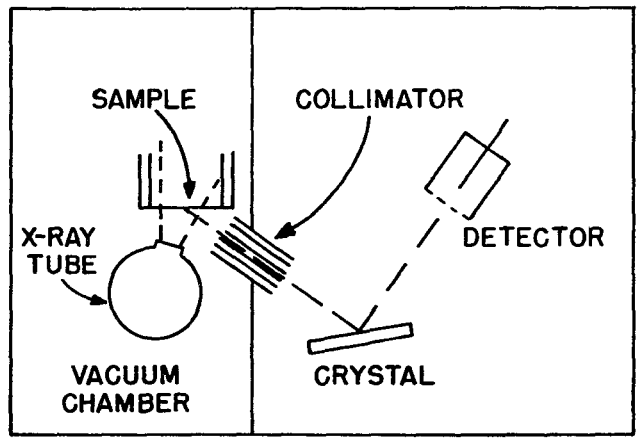

Fig. A-1 — Schematic of single-crystal, vacuum x-ray spectrometer

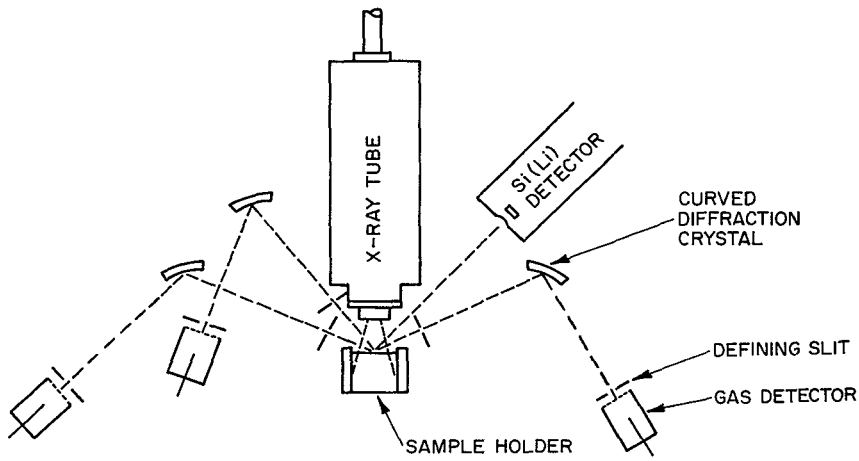

Fig. A-2 — Schematic of multi-spectrometer x-ray machine

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Naval Research Laboratory Washington, D.C. 10275	Unclassified
	2b. GROUP

3. REPORT TITLE

TRACE METAL WATER POLLUTANTS DETERMINED BY X-RAY FLUORESCENCE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

This is an interim report; work on this project is continuing.

5. AUTHOR(S) (First name, middle initial, last name)

Philip G. Burkhalter

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
August 7, 1973	20	12

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
NRL Problem 66P04-04 b. PROJECT NO.	NRL Report 7637
c. d.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Department of the Navy (Office of Naval Research), Arlington, Virginia 22217

13. ABSTRACT

X-ray fluorescence analysis was evaluated for determining trace metals in samples of interest in the Water Quality Control Program. A number of toxic elements including Pb were determined in Potomac River water and Blue Plains sewage sludge. Analysis by x-rays has sufficient detectability to determine both insoluble and soluble pollutants in river water and effluent waste.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Water pollution Trace metals X-ray fluorescence analysis						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE-2)

Security Classification